HALOGEN GEOCHEMISTRY OF UNOPENED ANGSA AND CONVENTIONAL APOLLO MATERIALS: THE 'END-MEMBER' OF VOLATILE PROCESSING? A.M. Gargano[1], J.I. Simon[2], C.K. Shearer[1,3,4], Z.D. Sharp[1], W. Buckley[5], and the ANGSA Science Team[6] [1]Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, 87131 (agargano@unm.edu), [2]Center for Isotope Cosmochemistry and Geochronology, ARES, NASA Johnson Space Center, Houston, TX 77058, USA, [3]Institute of Meteoritics, University of New Mexico, Albuquerque, 87131, [4] Lunar and Planetary Institute, Houston TX 77058,[5]Jacob-JETS Contract, NASA Johnson Space Center, Houston, TX 77058, USA, [6]ANGSA Science Team list at https://www.lpi.usra.edu/ ANGSA /teams/.

Motivation: Halogen geochemistry of planetary materials remains poorly understood due to a scarcity of available data. The Moon, which exhibits a uniquely large range in chlorine isotope compositions (δ^{37}Cl) from around -1 to +40‰ [1-4] potentially records the evolved halogen geochemistry 'end-member' produced by extensive planetary surface reprocessing. In our previous work, we measured the halogen contents and δ^{37}Cl values of lunar materials and found no significant relationships [4]. While we interpreted these data to suggest that the source of the Moon's chlorine isotope anomaly and relative halogen abundances was largely inherited from the Giant Impact – we have not fully explored the devolatilization processes associated with regolith maturation in terms of combining halogen contents and chlorine isotope compositions. Thus, we seek to better understand the processing of volatile elements in this near surface reservoir.

The lunar surface likely acted as a 'cold-sink' and experienced extensive reworking that resulted in volatile remobalization, and retains anomalous volatile-element stable isotope compositions for S, Cl, Zn and K. As such, this reservoir (represented by a several meter thick packets of regolith [5]) is potentially significant in understanding the source of the Moon's volatile element stable isotope anomalies.

The ANGSA mission is applying simultaneous novel elemental and isotopic characterizations on the same lunar samples for the first time. As we show in recent work [5], the comparisons of multiple volatile-element stable isotope compositions reveal complexity beyond simple kinetic isotope fractionation to space. Due to the unique storage conditions of the ANGSA core, some of the most difficult volatiles to constrain, such as hydrogen, will provide invaluable comparisons to chlorine isotope compositions and halogen contents. Here we present the halogen contents and chlorine isotope compositions of ANGSA soils and compare the data to that of [6], as well as new lunar data on impact melt splatters, breccias, and highlands rocks.

ANGSA vs. Apollo Soils Halogen Abundances and Isotopes: Figure 1 depicts the ranges of halogen ratios (F/Cl, Br/Cl, and I/Cl) of pertinent solar system and lunar reservoirs. Several broad trends can be seen in this dataset: 1) relative to carbonaceous and ordinary chondrites (CC, OC [7]) lunar materials exhibit markedly different averages and ranges of halogen ratios. 2) The range of individual halogen ratios is generally associated with halogen volatility, whereby, I ~ Br > Cl >> F. 3) Highlands and mare lithologies cluster with markedly higher F/Cl and I/Cl ratios driven by low Cl contents, presumably due to devolatilization. 4) The halogen ratios of ANGSA soils are largely similar from those of [6], albeit with lower Br/Cl ratios driven by low Br contents in ANGSA soils. 5) Br/Cl ratios are the most variable across lunar materials – likely resulting from Br mobility on the lunar surface [6]. Figure 2 shows the ranges of halogen contents of ANGSA soils relative to [6].

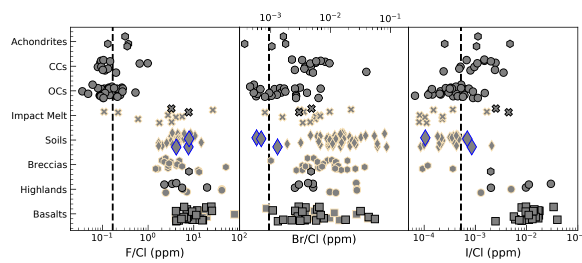

Figure 1 (left to right): F/Cl, Br/Cl, and I/Cl of planetary and lunar reservoirs. Data outlined in black are from Gargano et al., 2020 and this work. Data outlined in light grey are from a compilation from Jovanovic and Reed [5]. Black vertical line is the average halogen ratio of OCs including unpublished data [6]. Diamonds outlined in blue are ANGSA soils.

Processing of lunar regolith: Some of the overarching processes which control the volatile-element chemistry of lunar soils are as follows [8]: 1) Lunar soils largely represent the host-lithology they are formed from (i.e., Apollo 16 soils are dominated by highlands material). 2) Generally, fine fractions (<10 um) are enriched in friable materials such as plagioclase and mesostasis. 3) The 'agglutinate forming process' driven via impacts preferentially occurs in the fine fractions of soils resulting in the loss of Na and K (and presumably other similarly volatile-elements). 4) Lunar

soils also contain exogenous volatiles such as solar wind implanted hydrogen.

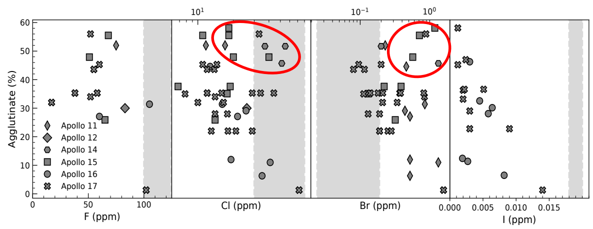

Figure 3: F, Cl, Br, and I contents vs. agglutinate content. Grey vertical bars are the ranges of halogen contents for ANGSA soils.

Are there distinct halogen reservoirs in the Moon?: It has been long suspected that particular interior reservoirs such as urKREEP contain distinctly high halogen contents [9], and nearly all Apollo 16 rocks present with some-degree of 'rust' which are interpreted to reflect a widespread vapor-deposition process and perhaps terrestrial modification of these deposits [10]. Despite this idea, A16 soils are not systematically enriched in F, Cl, Br, or I. These results are unexpected as such widespread vapor-deposition would presumably manifest as large halogen enrichments in the soils, which is not observed (Fig. 2). A feasible explanation as to why this is not seen is that the agglutinate-forming and soil maturation processes effectively depleted the initially halogen-rich source material, however, the question that then follows is where are these volatiles now stored? Presumably other volatiles could behave similarly to hydrogen, whereby it is thought to gradually migrate towards the lunar poles [11].

Chlorine isotope compositions of lunar soils: Of the scarce chlorine isotope measurements performed on lunar soils – several observations have been made: 1) lunar soils preserve the characteristically high δ^{37}Cl values of the Moon ranging from around 5-16‰ [1, 12]. 2) Akin to mare basalts, soils retain low δ^{37}Cl values in their water-soluble chloride fractions representative of the deposition of isotopically light chlorides from vaporization processes [1, 4, 5]. The ANGSA core rind was measured to have $\delta^{37}Cl_{SBC,\ WSC}$ values of 8.5 and 8.8‰, respectively with $[Cl]_{SBC,\ WSC}$ of 58 and 26 ppm, respectively. These δ^{37}Cl values are different from previous measurements on A16 soils (with $\delta^{37}Cl_{SBC,\ WSC}$ values of 64501: 15.7, 5.6‰ and 61120: 14.3, and 6.1‰). The $[Cl]_{SBC,\ WSC}$ of these samples are 8, 19, and 10, 16 ppm, respectively.

A unique mechanism for the fractionation of Cl isotopes in lunar soils has not been proposed; however, if we assume that minimal fractionation of Cl isotopes occurs throughout soil maturation (as shown by [12]), then these data may suggest a source-region difference in the dominant host-lithologies for the A16 (highlands) and A17 soils (high-Ti mare and Mg-suite). This idea would be generally consistent with the available bulk-rock δ^{37}Cl values, which show that highlands lithologies present a large range of δ^{37}Cl values from 10-30‰, whereas A17 samples are comparably restricted from 4-12‰ [4]. Conversely, given the high Cl contents of the ANGSA soil – it is also feasible that an isotopically light vapor has been effectively incorporated into this material which would generally serve to increase [Cl], and decrease δ^{37}Cl values (due to kinetic isotope fractionation). We stress, however, that this simplistic process could manifest differently as we have previously proposed for the ferroan anorthosites [4] in which late-stage vapor incorporation could increase [Cl] with increasing δ^{37}Cl values.

Conclusion and outlook: Lunar soils provide an invaluable data set for understanding surface processing on planetary bodies and potentially retain primary chemical characteristics of their source regions. The ANGSA mission is a dramatic step forward in applying several novel volatile-element chemical and isotopic techniques simultaneously on the same samples. We believe these interelement and isotopic characterizations will be helpful in revealing the cryptic volatile-element processing which occur on the Moon.

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